PART ONE
TRIMESITYLVINYL ALCOHOL

PART TWO
ADDITION OF GRIGNARD REAGENTS TO 2-METHOXYARONITRILES

BY

DAVID HENRY CHADWICK

B. S., University of New Hampshire, 1940

M. S., University of New Hampshire, 1942

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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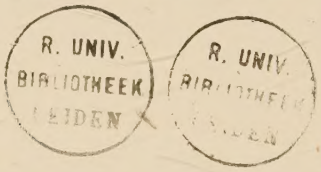
Acknowledgment

The author wishes to express his sincere appreciation to Professor Reynold C. Fuson for his suggestions and advice during the course of this investigation.



PART ONE

TRIMESITYLVINYL ALCOHOL

Introduction

The discovery of a group of stable enols (1,2,3) in which factors other than chelation of the enolic hydroxyl group with a *beta* carbonyl group must supply the stabilizing influence has led to an effort to define the structural features which confer their exceptional resistance to ketonization. The problem has been attacked by varying the number, nature, and position of mesityl-type radicals about the vinyl alcohol structure.

Although *cis-trans* isomerism should be possible with enols of this type, it has been observed only in their esters (4). Thus one isomer of each keto enol is unknown, as is the configuration of the known isomer.

It is therefore of interest to prepare a series of vinyl alcohols bearing like radicals of the *beta* position to preclude the possibility of *cis-trans* isomerism. Furthermore, by varying the radical placed in the *alpha* position of the enol, it should be possible to determine if a high degree of hindrance about the *beta* carbon atom will stability a ketone enol having no hindering group in the *alpha* position. Dimesitylketene provides a convenient route to this end.

Discussion and Results

By addition of methylmagnesium iodide, phenylmagnesium bromide, and mesitylmagnesium bromide to dimesitylketene it was possible to prepare, respectively, 1,1-dimesityl-1-propen-2-ol (I), 2,2-dimesityl-1-phenylvinyl alcohol (II) and trimesitylvinyl alcohol (III). Since these vinyl alcohols bear like substituents in the *beta* position, the possibility of *cis-trans* isomerism is precluded. They are, accordingly, the first keto vinyl alcohols of known configuration.

Vinyl alcohols I and II are the first ketone enols of this type which do not bear a hindering radical such as mesityl in the *alpha* position. 2,2-Dimesitylvinyl alcohol is known (5). Therefore, it now seems certain that a 2-2-dimesitylvinyl alcohol will be stable whether it bears an aromatic radical, an aliphatic radical, or a hydrogen atom in the *alpha* position.

Vinyl alcohol II was also prepared by the action of phenyllithium on dimesitylacetyl chloride. The ketone was prepared by condensation of dimesitylacetyl chloride and phenylmagnesium bromide. It was enolized by hot sodium ethoxide in alcohol.

Of the three new vinyl alcohols, only III resisted ketonization when treated with methanolic hydrogen chloride. All attempts to prepare the ketone by Friedel-Crafts type reactions produced only anomalous products. Attempted condensation of dimesitylacetyl chloride and mesitylmagnesium bromide was also unsuccessful. These results are attributed to the extreme space exigency within the molecule, as shown by models.

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PART TWO

ADDITION OF GRINARD REAGENTS TO 2-METHOXYARONITRILES

Introduction

The replacement of nuclear methoxyl groups by the use of the Grignard reagent was first realized in this laboratory (1,2). For example, 1-mesitoyl-2-methoxynaphthalene may be converted to 1-mesitol-2-ethylnaphthalene in high yield by the action of ethylmagnesium bromide. The reaction is believed to proceed through 1,4-addition of the Grignard reagent, followed by elimination of the elements of methanol.

Richtzenhain (3) has recently reported a similar replacement of nuclear alkoxyl groups by the action on ethylmagnesium bromide on 2,3-dimethoxybenzonitrile. Although Richtzenhain appears to recognize the probability that the mechanism is 1,4-addition of the Grignard reagent, he make no reference to the similar replacement observed with ketones, nor does he present experimental evidence to indicate such a course of reaction.

The present work was undertaken with the objective of extending this type of reaction of 2-methoxyaronitriles, and of obtaining evidence of the mechanism through which it proceeds.

Discussion of Results

In view of the high yields obtained in the replacement of the methoxyl group in 1-mesitoyl-2-methoxynaphthalene, 2-methoxynaphthonitrile was chosen for preliminary investigation. Due to stabilization of the bond structure of the naphthalene nucleus, 1,4-addition should be facilitated. Actually, the nitrile reacted with ethylmagnesium bromide or benzylmagnesium chloride in the 1,2-manner to produce imines.

Addition of ethylmagnesium bromide to 2,3-dimethoxybenzonitrile produced a compound having the composition of 2-ethyl-3-methoxybenzonitrile, as reported by Richtzenhain (3).

None of the desired 1,4-addition product could be obtained from the condensation of ethylmagnesium bromide with 2-methoxybenzonitrile, 2,6-dimethoxybenzonitrile, or 2-5-dimethoxybenzonitrile. A high yield of the imine resulting from 1,2-addition of the Grignard reagent was obtained in each case.

As yet, no satisfactory explanation has been presented for these surprising results.

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Vita

The author was born in Sutton, N. H., on August 8, 1918. He attended the elementary schools in that town and Simonds Free High School in Warner, N. H. He received the Bachelor of Science degree from the University of New Hampshire in 1940. He held a teaching assistantship at the University of New Hampshire during 1940-41, and was an Assistant durring 1941-42, receiving the Master of Science degree in May, 1942. During the summers of 1939, 1940, and 1941 he was employed as a research assistant by the Dennison Manufacturing Company of Framingham, Mass. In the summer of 1942 he enrolled in the Graduate School of the University of Illinois, where he held a teaching assistantship during the academic years of 1942-43, 1943-44, and 1945-46. He was employed on a National Defense Research Committee project operated by the Monsanto Chemical Company, Anniston, Ala., during the summer of 1943, and by the Clinton Engineer Works of the Tennessee Eastman Corporation, Oak Ridge, Tenn., from May, 1944, to October, 1945.

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